

16. (New) The method according to claim 10, wherein the starting substances are provided in the providing step in powder form.

17. (New) The method according to claim 10, wherein zirconia partially stabilized with 7% to 9% by weight of yttria is deposited in the depositing step.

18. (New) The method according to claim 10, wherein the thermal barrier coating is deposited in the depositing step on the component in a layer thickness of between 75  $\mu\text{m}$  and 250  $\mu\text{m}$ --.

### **REMARKS**

This Preliminary Amendment cancels, without prejudice, claims 1 to 12 in the underlying PCT Application No. PCT/DE99/04018. This Preliminary Amendment further cancels, without prejudice, claims 1 to 9 in the annex to the International Preliminary Examination Report and adds new claims 10 to 18. The new claims, inter alia, conform the claims to U.S. Patent and Trademark Office rules and do not add any new matter to the application.

In accordance with 37 C.F.R. § 1.121(b)(3), the Substitute Specification (including the Abstract, but without the claims) contains no new matter. The amendments reflected in the Substitute Specification (including Abstract) are to conform the Specification and Abstract to U.S. Patent and Trademark Office rules or to correct informalities. As required by 37 C.F.R. §§ 1.121(b)(3)(iii) and 1.125(b)(2), a Marked Up Version of the Substitute Specification comparing the Specification of record and the Substitute Specification also accompanies this Preliminary Amendment. Approval and entry of the Substitute Specification (including Abstract) is respectfully requested.

The underlying PCT Application No. PCT/DE99/04018 includes an International Search Report, dated April 28, 2000, a copy of which is included. The Search Report includes a list of documents that were considered by the Examiner in the underlying PCT application.

The underlying PCT Application No. PCT/DE99/04018 also includes an International Preliminary Examination Report dated February 23, 2001, an English translation of the annexed pages thereto are enclosed herewith.

It is respectfully submitted that the subject matter of the present application is new, non-obvious and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully submitted,

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## PROCESS FOR PRODUCING A THERMAL BARRIER COATING

FIELD OF THE INVENTION

The present invention relates to a process for producing a thermal barrier coating, in which organometal complexes of zirconium and at least one [stabilising] stabilizing element selected from the group of the alkaline earth metals or rare earths are provided as starting substances, the starting substances are evaporated by heating and the coating gases which are generated [in this way] are transported to a component to be coated, which is heated at a deposition temperature, where they are broken down so that a layer is deposited.

BACKGROUND INFORMATION

Electron beam physical [vapour] vapor deposition (EB-PVD) processes, in which the substances [which] that are to be deposited on the metallic component, such as, for example, zirconium oxide, are vaporized in a high-vacuum environment using an electron beam, are [known] conventionally used for the production of thermal barrier coatings. On account of the considerable introduction of energy, a thin, molten zone is formed, from which the substances are [vapourised] vaporized and, in a condensation reaction, are deposited on the surface of the component. The layers produced in this [way] manner have a columnar structure which tolerates expansion, is better able to withstand alternating temperature stresses and [leads to] results in a prolonged service life.

Drawbacks of these processes are the extremely high installation costs for the electron beam gun, for the generation of the high vacuum, for the vacuum chamber and for the partial pressure control. Furthermore, those surfaces of

the component [which] that are not directly visible cannot be coated or can only be insufficiently coated during the coating cycle.

5 [EP] European Published Patent Application No. 0 055 459 [A1 has disclosed] describes a process for producing oxide layers by [means of] chemical [vapour] vapor deposition (CVD), in which complexes derived from diketones, such as, for example, acetylacetonate complexes, are mixed with steam in order to  
10 [oxidise] oxidize the metals contained in the complexes and are deposited on a substrate. In the process, the substrate is heated in various applications to temperatures of between 350°C and 800°C. The thicknesses of the deposited layers are in the range between 3.6 and 34  $\mu\text{m}$ . The use of steam as a  
15 carrier gas has proven imperative, since oxygen does not enable either reproducibility or deposition to be achieved.

International Published Patent Application No. WO 94/21841  
[has disclosed] describes a flame CVD process for applying  
20 inorganic layers to substrates, in which mixed oxides, such as [yttrium-stabilised] yttrium-stabilized zirconia, are deposited at flame temperatures of [from] between 300°C [to] and 2800°C and pressures [which lie] that are well above ambient pressure. The starting substances for the coating  
25 gases are passed into the flame and, in a flame CVD process of this type, cannot be heated with a defined temperature cycle and transported to the substrate.

In [known] conventional processes for producing thermal  
30 barrier coatings by means of chemical [vapour] vapor deposition (CVD), it has [hitherto] only been possible to produce very thin layers with a low deposition rate and without a columnar structure, which layers also present poor adhesion and, moreover, contain relatively large quantities of  
35 undesirable carbon impurities. [With a view] Relative to

industrial use, the selection of the starting substances is of particular importance, since [on the one hand] they must not be too expensive and [on the other hand] they must be available in sufficient quantities.

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[The problem on which] It is an object of the present invention [is based consists in providing] to provide a process for producing a thermal barrier coating [of the generic type described in the introduction] in which a thermal barrier coating with [good] sufficient layer properties and a columnar structure is produced as inexpensively as possible.

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#### SUMMARY

According to one example embodiment of the present invention, [the solution to this problem is characterized in that] the starting substances are heated, at a process pressure of 0.5 to 50 mbar, to at most 250°C so that the coating gases are formed, and the coating gases are transported to the component to be coated, the surface of which is heated at a deposition temperature of between 300°C and 1100°C.

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[In this context, it has proven advantageous that thermal] Thermal barrier coatings [which] that contain zirconium oxide and, for example, yttrium oxide, [can] may be produced with a sufficiently [great] large layer thickness of approximately 25 to 1000 µm using the process [which] that is based on the chemical [vapour] vapor deposition (CVD) principle. Moreover, the thermal barrier coatings produced in this [way] manner have a suitable crystal structure and morphology and required layer properties. In terms of their ability to withstand alternating temperature stresses, the layers are comparable to those produced using the EB-PVD process. A further advantage is that, unlike in the electron beam physical [vapour] vapor deposition (EB-PVD) process, the scattering force of the process means that even those surfaces of the component to be

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coated [which] that are not directly visible [can] may be coated.

[In a preferred configuration, organometal] Organometal  
5 complexes, which are derived from diketones, of zirconium and  
at least one [stabilising] stabilizing element selected from  
the group consisting of the alkaline earth metals or rare  
earths are provided as starting substances, since with these  
components the coating gases are completely broken down or  
10 burnt when they come into contact with that surface of the  
component [which] that has been heated to deposition  
temperature. Moreover, they have the advantage over alkoxides  
that they are not sensitive to hydrolysis and are therefore  
easier to handle.

15 Furthermore, [it is preferable for] the coating gases [to] may  
be mixed with a carrier gas, such as, for example, oxygen or a  
mixture of oxygen and argon.

20 In a further [configuration] example embodiment of the process  
according to the present invention, the coating gases or the  
coating gases and the carrier gas [can] may be transported to  
the component to be coated, which is arranged in a receptacle,  
in an admission system [which] that has been heated to at most  
25 250°C.

[It has proven expedient for the] The process [to] may be  
[carried out] performed at a low process pressure of 0.5 to 50  
mbar, in order that the coating gases or the coating gases and  
30 the carrier gas are transported as quickly as possible, so  
that their residence time in the hot zone produced by the  
thermal radiation of the component or substrate [which] that  
has been heated to the deposition temperature is as short as  
possible and to [minimise vapour] minimize vapor phase  
35 reactions.

Yttrium, lanthanum, calcium, magnesium or cerium [are preferably] may be provided as the [stabilising] stabilizing element from the group consisting of the alkaline earth metals or rare earths, since they are not excessively expensive with regard to process costs and, furthermore, are available in sufficient quantities for industrial use. [

Further configurations of the invention are described in the subclaims.

In the text which follows, the invention is explained in more detail on the basis of exemplary embodiments and with reference to a drawing, in which:]

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 [shows] is a [diagrammatic sectional] schematic cross-sectional view through a thermal barrier coating [which] that has been produced using one [exemplary] example embodiment of the process according to the present invention[, and].

Fig. 2 [shows] is a microscopic image of a thermal barrier coating [which] that has been produced using an [exemplary] example embodiment of the process according to the present invention, in which image a columnar structure [can] may be [recognised] recognized.

#### DETAILED DESCRIPTION

Fig. 1 [shows] illustrates a thermal barrier coating[, which is denoted overall by] 1 [and], which has a columnar structure 2, i.e., a fringe crystal structure, which has been deposited on a substrate 4 provided with an adhesion layer 3. In the present [exemplary] example embodiment, the substrate 4 is a surface of a metallic rotor blade of a gas turbine around which hot gases flow in operation. Alternatively, the process [can] may also be used, for example, to coat guide vanes of

gas turbines or other parts of internal-combustion engines which are exposed to hot gases.

In the present [exemplary] example embodiment of the process for producing a thermal barrier coating by [means of] chemical [vapour] vapor deposition (CVD), [first of all] an adhesion layer 3 is applied to the surface of the rotor blade 4 around which hot gases flow using a conventional process. The adhesion layer 3 [is preferably] may be able to resist corrosion from hot gases and may, for example, be an [aluminium] aluminum diffusion layer, a [platinum/aluminium] platinum/aluminum diffusion layer or an MCrAlY cladding layer.

Then, the starting substances for the deposition of the thermal barrier coating 1 by [means of] chemical [vapour] vapor deposition (CVD) are provided.

Acetylacetonate complexes of zirconium and yttrium [which] that are [in each case] in powder form and are mixed in the appropriate ratio to form the desired layer stoichiometry are selected for these materials. Alternatively, the starting substances may also be [vapourised] vaporized separately and mixed in the [vapour] vapor phase. The starting substances are [vapourised] vaporized or converted into the [vapour] vapor phase by being heated to at most 250°C, so that the coating gases are formed, and are transported to the rotor blades 4 to be coated. They are transported by [means of] suitable carrier gases, such as, for example, oxygen or a mixture of oxygen and argon.

Moreover, those surfaces of the rotor blades 4 [which] that are to be coated are heated, by [means of] a suitable heat source, at a deposition temperature of between 300°C and 1100°C. This ensures that the coating gases are not heated to over 250°C on their flow path to the rotor blades 4 to be



coated. This is effected by, for example, using an admission system [which] that has been heated to at most 250°C and is arranged so as to take account of the heat sources for the components or rotor blades 4, through which system the coating gases and the carrier gas are transported to that surface of the rotor blade 4 [which] that is to be coated.

In the vicinity of those surfaces of the rotor blades 9 [which] that have been heated to the deposition temperature, it may be impossible to completely prevent the coating gases from being heated to this extent [on account of] due to thermal radiation. In order to suppress the [vapour] vapor phase reactions of the coating gases [which] that are possible at elevated temperatures, the thermal barrier coating 1 is produced or deposited at relatively low process pressures of 0.5 to 50 mbar, so that they have a short residence time in the hot zones around the rotor blades 4 [which] that have been heated to deposition temperature. To achieve the low process pressure required for the present [vapour] vapor phase deposition, the process is [carried out] performed in a closed receptacle, to which a pump is connected.

When the coating gases come into contact with those surfaces of the rotor blades 4 [which] that have been heated to deposition temperature, the chemical decomposition of the starting substances occurs and [yttria-stabilised] yttria-stabilized zirconia is deposited so as to form the thermal barrier coating 1 and gaseous by-products. Complete decomposition [takes place on account of] occurs due to the high deposition temperatures. There are [scarcely any] substantially no carbon impurities. Furthermore, the thermal barrier coating 1 [which] that has been deposited has a columnar structure 2 or fringe crystal structure [which] that is able to tolerate expansion and is of benefit to the resistance to alternating temperature stresses and to the

service life of the thermal barrier coating 1. In the  
[present] process according to the present invention, the  
scatter [which] that is achieved by [exploitation of] use of  
the aerodynamic flow conditions [means that] results in not  
5 only those surfaces of the rotor blades 4 [which] that are  
directly visible or exposed to flow, but also all of the other  
surfaces [which] that are exposed to the flow of the coating  
gases and have been heated, are coated. The by-products are  
broken down in a downstream pyrolysis furnace and are then  
10 filtered and disposed [off] of.

To improve the uniformity of coating, the rotor blades 4 may  
be moved inside the receptacle. Depending on how the process  
is controlled, it is possible to deposit thermal barrier  
15 coatings 1 with a layer thickness of approximately 25 to 1000  
 $\mu\text{m}$  on the surfaces of the rotor blades 4, the layer thickness  
generally [lying] being between 75 and 250  $\mu\text{m}$ . Compared to  
rotor blades, the thermal barrier coatings 1 deposited on  
guide vanes of gas turbines often have higher layer  
20 thicknesses. To form the thermal barrier coatings 1,  
deposition in the present uses zirconia partially stabilized  
with 7-9% by weight of yttria. The process [can] may be used  
for all parts of a gas turbine or other internal-combustion  
engines [which] that are exposed to hot gases.

[Abstract] ABSTRACT

A process for producing a thermal barrier coating, in which organometal complexes of zirconium and at least one  
5 [stabilising] stabilizing element selected from the group of the alkaline earth metals or rare earths are provided as starting substances, the starting substances are evaporated by heating and the coating gases [which] that are generated in  
10 this [way] manner are transported to a component [(4)] to be coated, which is heated at a deposition temperature, where they are broken down so that a layer [(1)] is deposited, in which process, in order to produce a thermal barrier coating [(1)] with a columnar structure and a sufficient layer  
15 thickness, the starting substances are heated, at a process pressure of 0.5 to 50 mbar, to at most 250°C so that the coating gases are formed, and the coating gases are transported to the component [(4)] to be coated, the surface of which is heated at a deposition temperature of between 300°C and 1100°C [(Fig. 1)].